

PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

To:

KIM, Seong-Ki
9th Teheran Bd.
825-33, Yoksam-dong
Kangnam-ku
Seoul 135-080
RÉPUBLIQUE DE CORÉE

Date of mailing (day/month/year) 20 September 2001 (20.09.01)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference OPP007030KR	
International application No. PCT/KR00/01470	International filing date (day/month/year) 15 December 2000 (15.12.00)

1. The following indications appeared on record concerning:		
<input checked="" type="checkbox"/> the applicant	<input type="checkbox"/> the inventor	<input type="checkbox"/> the agent
<input type="checkbox"/> the common representative		
Name and Address LG CHEMICAL LTD. LG Twin Tower Yoido-dong 20 Yongdungpo-ku Seoul 150-721 Republic of Korea	State of Nationality KR	State of Residence KR
	Telephone No. +82 42 866 2070	
	Facsimile No. +82 42 863 2053	
	Teleprinter No.	
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:		
<input checked="" type="checkbox"/> the person	<input type="checkbox"/> the name	<input type="checkbox"/> the address
<input type="checkbox"/> the nationality		
<input type="checkbox"/> the residence		
Name and Address LG CHEMICAL CO., LTD LG Twin Tower Yoido-dong 20 Yongdungpo-ku Seoul 150-721 Republic of Korea	State of Nationality KR	State of Residence KR
	Telephone No. +82 42 866 2070	
	Facsimile No. +82 42 863 2053	
	Teleprinter No.	
3. Further observations, if necessary:		
4. A copy of this notification has been sent to:		
<input checked="" type="checkbox"/> the receiving Office	<input checked="" type="checkbox"/> the designated Offices concerned	
<input type="checkbox"/> the International Searching Authority	<input type="checkbox"/> the elected Offices concerned	
<input type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:	

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Idhir BRITEL
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

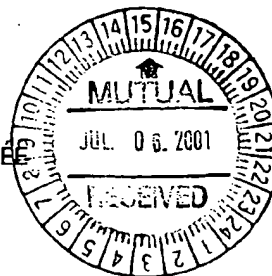
PCT

NOTICE INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

KIM, Seong-Ki
9th Teheran Bd.
825-33, Yoksam-dong
Kangnam-ku
Seoul 135-080
RÉPUBLIQUE DE CORÉE

Date of mailing (day/month/year) 21 June 2001 (21.06.01)		
Applicant's or agent's file reference OPP007030KR		IMPORTANT NOTICE
International application No. PCT/KR00/01470	International filing date (day/month/year) 15 December 2000 (15.12.00)	
Priority date (day/month/year) 15 December 1999 (15.12.99)		
Applicant LG CHEMICAL LTD. et al		

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:

AU,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

CN,EP,IN,JP,SG

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 21 June 2001 (21.06.01) under No. WO 01/44113

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

PCT REQUEST

OPP007030KR

Duplicate of original printed on 15.12.2000 11:35:05 AM

0	For receiving Office use only	
0-1	International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4	Form - PCT/RO/101 PCT Request	
0-4-1	Prepared using	PCT-EASY Version 2.91 (updated 10.10.2000)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	Korean Industrial Property Office (RO/KR)
0-7	Applicant's or agent's file reference	OPP007030KR
I	Title of invention	A METHOD FOR PREPARING LITHIUM MANGANESE SPINEL OXIDE HAVING IMPROVED ELECTROCHEMICAL PERFORMANCE
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	LG CHEMICAL LTD.
II-5	Address:	LG Twin Tower, Yoido-dong 20, Yongdungpo-ku, 150-721 Seoul Republic of Korea
II-6	State of nationality	KR
II-7	State of residence	KR
II-8	Telephone No.	+82 42 866 2070
II-9	Facsimile No.	+82 42 863 2053
III-1	Applicant and/or inventor	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	PARK, Hong-Kyu
III-1-5	Address:	LG Apt. 5-103, Doryong-dong 381-42, Yousung-ku, 305-340 Taejeon-city Republic of Korea
III-1-6	State of nationality	KR
III-1-7	State of residence	KR

PCT REQUEST

OPP007030KR

Duplicate of original printed on 15.12.2000 11:35:05 AM

III-2	Applicant and/or inventor	
III-2-1	This person is:	applicant and inventor
III-2-2	Applicant for	US only
III-2-4	Name (LAST, First)	BAE, Joon-Sung
III-2-5	Address:	LG Apt. 6-402, Doryong-dong 381-42, Yousung-ku, 305-340 Taejeon-city Republic of Korea
III-2-6	State of nationality	KR
III-2-7	State of residence	KR
III-3	Applicant and/or inventor	
III-3-1	This person is:	applicant and inventor
III-3-2	Applicant for	US only
III-3-4	Name (LAST, First)	PARK, Seong-Yong
III-3-5	Address:	LG Dormitory 515, Doryong-dong, Yousung-ku, 305-340 Taejeon-city Republic of Korea
III-3-6	State of nationality	KR
III-3-7	State of residence	KR
III-4	Applicant and/or inventor	
III-4-1	This person is:	applicant and inventor
III-4-2	Applicant for	US only
III-4-4	Name (LAST, First)	LEE, Ki-Young
III-4-5	Address:	LG Apt. 8-510, Doryong-dong, Yousung-ku, 305-340 Taejeon-city Republic of Korea
III-4-6	State of nationality	KR
III-4-7	State of residence	KR
IV-1	Agent or common representative; or address for correspondence	
	The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	KIM, Seong-Ki
IV-1-2	Address:	9th Teheran Bd., 825-33, Yoksam-dong, Kangnam-ku, 135-080 Seoul Republic of Korea
IV-1-3	Telephone No.	+82 2 3458 0800
IV-1-4	Facsimile No.	+82 2 539 0758
IV-1-5	e-mail	email@mutualip.com

PCT REQUEST

OPP007030KR

Duplicate of original printed on 15.12.2000 11:35:05 AM

V	Designation of States		
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE TR and any other State which is a Contracting State of the European Patent Convention and of the PCT	
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AU CN IN JP SG US	
V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.		
V-6	Exclusion(s) from precautionary designations	NONE	
VI-1	Priority claim of earlier national application		
VI-1-1	Filing date	15 December 1999 (15.12.1999)	
VI-1-2	Number	1999-58066	
VI-1-3	Country	KR	
VII-1	International Searching Authority Chosen	Austrian Patent Office (ISA/AT)	
VIII	Check list	number of sheets	electronic file(s) attached
VIII-1	Request	4	-
VIII-2	Description	12	-
VIII-3	Claims	3	-
VIII-4	Abstract	1	ab007030kr.txt
VIII-5	Drawings	6	-
VIII-7	TOTAL	26	
VIII-8	Accompanying items	paper document(s) attached	electronic file(s) attached
VIII-8	Fee calculation sheet	✓	-
VIII-9	Separate signed power of attorney	✓	-
VIII-12	Priority document(s)	Item(s) VI-1	-
VIII-16	PCT-EASY diskette	-	diskette
VIII-18	Figure of the drawings which should accompany the abstract	1	
VIII-19	Language of filing of the international application	English	

PCT REQUEST

OPP007030KR

Duplicate of original printed on 15.12.2000 11:35:05 AM

IX-1	Signature of applicant r agent	
IX-1-1	Name (LAST, First)	KIM, Seong-Ki

**FOR RECEIVING OFFICE USE ONLY**

10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/AT
10-6	Transmittal of search copy delayed until search fee is paid	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
------	--	--

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
21 June 2001 (21.06.2001)

PCT

(10) International Publication Number
WO 01/44113 A1(51) International Patent Classification⁷: C01G 45/12,
45/00, C01D 15/00, H01M 10/00, 4/50, 4/58

(21) International Application Number: PCT/KR00/01470

(22) International Filing Date:
15 December 2000 (15.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1999/58066 15 December 1999 (15.12.1999) KR(71) Applicant (for all designated States except US):
LG CHEMICAL LTD. [KR/KR]; LG Twin Tower,
Yoido-dong 20, Yongdungpo-ku, Seoul 150-721 (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): PARK, Hong-Kyu
[KR/KR]; LG Apt. 5-103, Doryong-dong 381-42,Yousung-ku, Taejeon-city 305-340 (KR). BAE,
Joon-Sung [KR/KR]; LG Apt. 6-402, Doryong-dong
381-42, Yousung-ku, Taejeon-city 305-340 (KR). PARK,
Seong-Yong [KR/KR]; LG Dormitory 515, Doryong-dong,
Yousung-ku, Taejeon-city 305-340 (KR). LEE, Ki-Young
[KR/KR]; LG Apt. 8-510, Doryong-dong, Yousung-ku,
Taejeon-city 305-340 (KR).(74) Agent: KIM, Seong-Ki; 9th Teheran Bd., 825-33, Yok-
sam-dong, Kangnam-ku, Seoul 135-080 (KR).

(81) Designated States (national): AU, CN, IN, JP, SG, US.

(84) Designated States (regional): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: A METHOD FOR PREPARING LITHIUM MANGANESE SPINEL OXIDE HAVING IMPROVED ELECTROCHEMICAL PERFORMANCE

(57) Abstract: The present invention relates to a method for preparing a lithium manganese complex oxide $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0 < x < 0.12$) used as a cathode active material of a lithium or lithium ion secondary battery. The present invention provides a method for preparing a manganese compound comprising the step of simultaneously applying a mechanical force and heat energy to a manganese compound to remove defects present in particles of the manganese compound and to control the aggregation of particles and the shape of the aggregated particles, a method for preparing a lithium manganese complex oxide with a spinel structure using the manganese compound prepared by the above method as a raw material, and a lithium or lithium ion secondary battery using the lithium manganese complex oxide with a spinel structure prepared by the above method as a cathode active material. A lithium or lithium ion secondary battery using the lithium manganese complex oxide with a spinel structure prepared from the manganese compound without defects inside particles as a cathode active material has excellent charge/discharge characteristics and cyclic performance.

WO 01/44113 A1

A METHOD FOR PREPARING LITHIUM MANGANESE SPINEL OXIDE HAVING IMPROVED ELECTROCHEMICAL PERFORMANCE

BACKGROUND OF THE INVENTION

(a) Field of the Invention

5 The present invention relates to a method for preparing lithium manganese complex oxide, $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0 \leq x \leq 0.12$), with a spinel structure used for a cathode active material of a lithium or lithium ion secondary battery.

(b) Description of the Related Art

10 LiCoO_2 compound is most commonly used for a cathode active material of a lithium or lithium ion secondary battery having an electric potential of 4 V (voltage). However, many studies for other active materials have been conducted recently, because LiCoO_2 compound is expensive and disadvantageous in terms of stability. A lithium manganese complex oxide,
15 $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0 \leq x \leq 0.12$), with a spinel structure, is one of the most actively studied materials, because it is inexpensive and stable during its usage, and it has an environmental affinity.

 The conventional method for synthesizing lithium manganese complex oxide with a spinel structure comprises mixing a manganese
20 compound and a lithium compound so as to adjust their chemical compositions, and heat-treating the mixture at a high temperature. USP 5,718,877 discloses a heat-treatment process for obtaining chemically uniform spinel, and R. J. Gummow et al., Solid State Ionics, 69, 59(1994) state that a compound with a spinel structure is not limited to the
25 stoichiometry of LiMn_2O_4 , and a spinel structure forms even if x in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ varies from 0 to 0.33, and, as x increases, the valence of Mn reaches 4 and the crystalline structure becomes stabilized.

 After it was reported that the deterioration of electrochemical

characteristics of lithium manganese complex compound with a spinel structure is promoted by nonuniformity of spinel composition, various studies for synthesizing more chemically uniform spinel using a liquid phase method have been attempted. However, with most liquid phase methods, a spinel compound having a particle size of several μm or less is obtained. Such micro particles are difficult to use as a cathode active material of a battery, because they have poor particle flow characteristics, charge density, tap density, and wettability for solvent, and thus they have many problems in the electrode preparation process, even if each particle has excellent electrochemical properties.

Recently, it was found that defects in raw materials, particularly electrolytic manganese dioxide (EMD), promote nonuniformity of the composition or local defects of structure when synthesizing spinel, and deteriorate the electrochemical properties of spinel. Inside EMD, a raw material of manganese, a variety of defects introduced during the process of synthesis (impurities, absorbed water, crystalline water, hydrogen ions, and other ions such as SO_4^{2-} , Cl , NH_4^+ , etc.) exist. Such impurities form a stable mesophase that exists as impurities during the heat-treatment process for obtaining the spinel compound of $\text{Li}_{1-x}\text{Mn}_{2-x}\text{O}_4$. In addition, such defects may deteriorate performance when used as a cathode active material of a lithium or lithium ion secondary battery, because the synthesized compound has internal lattice defects, even if it has a spinel structure. Specifically, lithium diffuses into a lattice of a spinel compound when charging/discharging, and the partial lattice defects inhibit the movement of lithium in the process of insertion and deintercalation, as well as react with lithium to decrease the amount of movable lithium, and consequently decreases the capacity of the battery.

There have been many attempts at removing the above-mentioned defects. The most representative method is acid treating or base treating the raw material powder in a strong acid or a strong base. The acid

3

treatment method is used to remove impurity metal ions existing in the raw material, and the base treatment method is used to substitute hydrogen ions in the raw material with lithium. Since these methods are used with aqueous solutions, they involve the risk of moisture infiltration into the raw material and the absorbed water may be incorporated therein. In addition, since particles strongly aggregate after they are dried of the aqueous solution, the above methods involve a pulverizing process, during which process the impurities may be incorporated again, and they have the inconvenience that an acid treatment cannot be conducted simultaneously with a base treatment to remove the impurities.

Another inherent problem is the shape of the secondary aggregate of the manganese raw material. When the mixture of manganese dioxide and lithium compound is heat-treated, lithium infiltrates the manganese compound and a reaction proceeds, and the shape of the formed spinel nearly maintains the shape of the particle of manganese raw material. Therefore, in order to control the shape of the spinel particle, the shape of the particle of manganese dioxide should be controlled.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method of preparing a manganese compound having an improved secondary aggregate shape without defects existing in the particles of the manganese compound raw material, in order to obtain a lithium manganese complex oxide with a spinel structure having improved performance, considering the above-mentioned problems of the prior art.

It is another object of the present invention to provide a method of preparing a lithium manganese spinel having improved performance using a manganese compound prepared according to the above method, which has improved particle shape and which does not have internal defects, as the manganese raw material.

It is another object of the present invention to provide a lithium or lithium ion secondary battery having improved electrochemical characteristics using a lithium manganese complex oxide with a spinel structure having improved performance, prepared according to the above method, that is obtained from the manganese compound that has improved particle shape and which does not have internal defects, as a cathode active material.

In order to achieve these objects, the present invention provides a method of preparing a manganese compound that is a raw material for a lithium manganese complex oxide, comprising the step of simultaneously applying a mechanical force and a heat energy to a manganese compound to remove defects present in particles of said manganese compound, and to control the aggregation of particles and the shape of the aggregated particles.

The present invention also provides a method of preparing lithium manganese complex oxide with a spinel structure, comprising the steps of (a) mixing (i) a manganese compound prepared according to the method comprising the step of simultaneously applying a mechanical force and a heat energy to remove defects present inside particles of a manganese compound and to control the aggregation of particles and the shape of the aggregated particles, and (ii) a lithium compound; and (b) calcinating the mixture obtained in said step (a).

The present invention also provides a lithium or lithium ion secondary battery comprising a lithium anode, an electrolyte and a cathode using lithium manganese complex oxide powder with a spinel structure as an active material, wherein said cathode active material is lithium manganese complex oxide with a spinel structure that is prepared by the method comprising the steps of (a) mixing (i) a manganese compound prepared according to the method comprising the step of simultaneously applying a mechanical force and a heat energy to remove defects present inside particles of said manganese compound and to control the aggregation of

particles and the shape of the aggregated particles, and (ii) a lithium compound; and (b) calcinating the mixture obtained in said step (a).

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the result of analyzing the distribution of defects present in the particles of MH-treated manganese dioxide using a thermal weight analyzer, according to the amount of time of MH treatment.

Figure 2 shows the change of the average valence of Mn in MH-treated manganese dioxide raw material, according to the amount of time of MH treatment.

Figure 3 shows a scanning electron microscope (SEM) photograph enlarged 500-fold expressing the shape of particles of manganese dioxide before MH treatment.

Figure 4 shows a scanning electron microscope (SEM) photograph enlarged 500-fold expressing the shape of particles of manganese dioxide after MH treatment.

Figure 5 shows the size of manganese dioxide particles before and after MH treatment and the distribution thereof.

Figure 6 shows the true density of lithium manganese spinel synthesized using MH-treated raw material, according to the amount of time of MH treatment.

Figure 7 shows the tap density of lithium manganese spinel synthesized using the MH-treated raw material of Example 1 and Example 2, according to the amount of time of MH treatment.

Figure 8 shows the charge/discharge characteristics of batteries of Example 1, Example 2 and Comparative Example.

Figure 9 shows the life characteristics of batteries of Example 1, Example 2 and Comparative Example.

Figure 10 shows a typical mechanofusion mill, wherein reference numeral 1 indicates a mixing chamber, 2 indicates a chamber wall, 3 indicates a fixing axis, 4 indicates the direction of chamber rotation, 5

6

indicates a thermoelectric zone, 6 indicates a scraper and 7 indicates an external heater.

DETAILED DESCRIPTION AND THE PREFERRED EMBODIMENTS

The present invention prepares a manganese compound that is a raw material for a lithium manganese complex oxide by applying a mechanical force and a heat energy to remove defects present inside particles of the manganese compound, prepares a lithium manganese complex oxide with a spinel structure using said manganese compound, and provides a lithium or lithium ion secondary battery using said lithium manganese complex oxide with a spinel structure as a cathode active material.

In the present invention, the operation of applying mechanical force and heat energy is referred to as "MH treatment". The mechanical force is applied to a particle of manganese compound raw material, and it produces strain in the aggregated particle to increase driving force that can rearrange the atoms according to their movement. Simultaneously, heat is applied to promote the rearrangement and evaporate absorbed water, water of crystallization, hydrogen ions and other evaporable ions present inside the secondary particles of the raw material.

Such MH treatment may decrease the concentration of defects present in the particles of the manganese compound, thereby increasing the average valence of Mn therein.

The results of MH treatment are proved by the following explanations of the drawings.

Figure 1 shows the results of analyzing the defects in the particles before and after MH treatment using a thermal gravimetry analyzer, indicating that the total defects largely decrease after MH treatment compared to those before MH treatment.

Figure 2 shows the average valence of the Mn according to the amount of time of MH treatment, and indicates that, as the amount of time of

MH treatment increases, the valence increases. This is because the volatile ions that exist as impurities such as NH_4^+ , H_3O^+ , etc. are discharged to increase the valence of Mn.

Figures 3 and 4 show the shapes of manganese dioxide particles before and after MH treatment, respectively, as seen through a SEM, indicating that the shape drastically changes.

Figure 5 shows the result of analyzing the size of manganese dioxide particles before and after MH treatment and the distributions thereof using a grading analyzer, indicating that after MH treatment, the size of manganese dioxide secondary particles is suitable for use as a cathode active material.

Such MH treatment of the present invention can be conducted using a specific apparatus that can apply shear stress to the surface of particles, such as a ball mill, attrition mill, jet mill, centrifugal mill, etc., to which a heating apparatus is attached. Such shear stress applies stress to particles to increase a driving force for the movement of atoms in the material, and simultaneously, a heat energy evaporates volatile impurities while promoting the movement of material.

A preferable example of said apparatus is surface coating apparatus called "a mechanofusion mill" as used in the Example of the present invention. Said apparatus has the advantage of being capable of applying mechanical force such as shear stress, compression stress, etc. to a particle and externally controlling the temperature, and it is generally used for coating fine metal on ceramic powder. The principle of the operation of said apparatus is shown in Fig. 10. Specifically, the manganese compound raw material, is introduced into the mixing chamber (1), and the manganese compound gathers along the rotating chamber wall (2) by centrifugal force and receives shear stress and compression stress at the fixing axis (3). The scraper (6) scrapes the manganese compound attached to the chamber wall (2), and the thermoelectric zone (5) controls heating of the outer heater (7).

In the present invention, manganese dioxide such as electrolytic manganese dioxide (EMD; MnO_2) and chemical manganese dioxide (CMD; MnO_2), Mn_2O_3 and Mn_3O_4 can be used as the raw material.

The mechanical force applied to said manganese compound is preferably approximately 0.1 to 1000 dyne/cm², in which range the three-dimensional destruction of the aggregated particles does not occur. Since mechanical energy removes edge parts of the raw material to make it globular, when preparing an electrode from lithium manganese spinel complex oxide that is prepared using a MH-treated manganese compound as a raw material, the surface friction between particles decreases and the true density can be improved. The amount of time of applying mechanical energy and heat energy is preferably 5 minutes to 5 hours. If the time exceeds 5 hours, the particle shape of the prepared manganese compound becomes more spherical, but the disadvantages in terms of operating cost and time are too high. If the time is less than 5 minutes, it is difficult to sufficiently remove defects. The temperature range of heat energy is preferably 50 to 200 °C.

In said MH-treatment, preparations that make the treatment easy can be added. Preferable preparations include a lithium salt such as LiOH , $\text{LiOH} \cdot \text{H}_2\text{O}$, LiCH_3COO , LiCHO_2 , $\text{LiCHO}_2 \cdot \text{H}_2\text{O}$, LiNO_3 , and $\text{Mn}(\text{CH}_3\text{CO}_2)_2$, $\text{Mn}(\text{NO}_3)_2$ having a melting point of less than 200°C, and mixtures of other metal compounds and the above compounds. The amount of the preparations is preferably 0 to 20 wt% of the treated manganese compound. In addition, in a method of preparing lithium manganese complex oxide $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0 < x < 0.12$) with a spinel structure comprising the steps of mixing lithium compound and said manganese compound and calcinating the mixture, said lithium compound is preferably selected from a lithium salt group consisting of LiOH , $\text{LiOH} \cdot \text{H}_2\text{O}$, LiCH_3COO , LiCHO_2 , $\text{LiCHO}_2 \cdot \text{H}_2\text{O}$ and LiNO_3 . In addition, the temperature of calcination is 400 to 900 °C, and the time of calcinations is 1 to 30 hours.

The lithium manganese complex oxide with a spinel structure of the present invention is applied to a cathode active material of a lithium battery or lithium ion battery by mixing lithium manganese spinel compound powder in n-methyl pyrrolidine (NMP) solvent using graphite as a conductor and polyvinylidenedifluoride (PVDF) as a binder to prepare a slurry, coating said slurry on aluminum foil by a casting method, drying said slurry to prepare a cathode, and applying said cathode to a lithium secondary battery together with an anode and an electrolyte. Thus obtained battery has much better charge/discharge characteristics and life characteristics than a battery using a lithium manganese spinel compound prepared from the non MH-treated manganese compound of the prior art as a cathode active material.

The present invention will be explained in more detail with reference to the following Examples and Comparative Examples. However, the Examples are to illustrate the present invention, and the present invention is not limited to them.

[Example]

Example 1

MH treatment of manganese compound raw material

In order to remove defects present in electrolytic manganese dioxide (EMD; MnO_2), EMD was MH-treated. Specifically, the weight of MnO_2 raw material was quantified, and the quantified amount of MnO_2 was introduced into a mechanofusion mixer (Japan Kosokawa Company product AM-15) shown in Fig. 10, and shear stress and compression stress were applied to the particles of the raw material while applying 100°C of heat thereby preparing the modified manganese dioxide.

The change of the distribution of defects present in the particles of MH-treated manganese dioxide (surface absorption, volatile ions, crystalline water, or structural defects) according to the amount of time of MH treatment is shown in Fig. 1.

In addition, the change of the average valence of the Mn according to

the amount of time of MH treatment is shown in Fig. 2.

In addition, SEM photographs of the shapes of the particles before and after MH treatment are shown in Figs. 3 and 4, and the size of the particles and the distribution of the size analyzed by particle size analyzer are shown in Fig. 5.

The preparation of lithium manganese complex oxide with a spinel structure

The prepared MH-treated manganese dioxide raw material was mixed with lithium hydroxide monohydrate ($\text{LiOH} \cdot \text{H}_2\text{O}$) while controlling the ratio of Mn/Li to 0.538.

The sufficiently mixed powder was heat-treated in a furnace at 400 to 500 °C under an air atmosphere for 7 hours.

The heat-treated powder was cooled and then mixed again in order to make the chemical composition uniform.

Thus obtained powder was secondarily heat treated in a furnace at 750°C under an air atmosphere to synthesize lithium manganese spinel powder.

The change of the true density of manganese dioxide in the prepared spinel powder according to the amount of time of MH treatment is shown in Fig. 6, and the change of the tap density of manganese dioxide according to the time of MH treatment is shown in Fig. 7.

The application as a cathode active material and the evaluation of the battery characteristics

The prepared lithium manganese spinel compound powder was used as a cathode active material to prepare an electrode. Graphite was used as a conductor and polyvinylidenedifluoride (PVDF) was used as a binder. The weight ratio of the active material, conductor and binder was 85:10:5.

A binder was dissolved in n-methyl pyrrolidinone (NMP) and then an active material and a conductor were added to prepare a slurry.

The prepared slurry was coated on aluminum foil by a tape casting

method, and then it was dried in a vacuum drier at 130 °C for 2 hours to prepare a cathode.

Lithium metal was used as an anode. The cathode and the anode were cut to an appropriate size, and then a lithium ion secondary battery was constructed as a coin cell. 1 mole of LiPF_6 solution was used as an electrolyte, and the mixed solution of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) in the ratio of 1:2 was used as an electrolytic liquid.

The prepared cell was represented by $[\text{LiMnO}_2/\text{LiPF}_6\text{B}(1\text{M}) \text{ in EC} + 2\text{EMC/Li}]$. The charge/discharge characteristics and the life characteristics of the cell were evaluated. The evaluation of the capacity was conducted at the range of the charge/discharge voltage of 3.0 to 4.5 V, and the evaluation of the life characteristics was conducted at the range of 3.4 to 4.3 V.

The charge/discharge characteristics are shown in Fig. 8, and the life characteristics are shown in Fig. 9.

Example 2

MH treatment of manganese compound raw material

EMD was MH treated by the same method as described in Example 1, except that 0.03 mole of $\text{LiOH} \cdot \text{H}_2\text{O}$ per 1 mole of MnO_2 was further added as a preparation to enhance MH treatment.

The preparation of lithium manganese complex oxide with a spinel structure

Lithium manganese spinel was prepared by the same method as described in Example 1, except that MH-treated EDM to which said preparation was added was used.

The change of tap density of manganese dioxide in the prepared spinel powder according to the time of MH treatment is shown in Fig. 7.

The application as a cathode active material and the evaluation of the battery characteristics

A battery was prepared by the same method as described in Example 1,

12

except that lithium manganese spinel prepared in the above was used as a cathode active material, and the characteristics thereof were evaluated.

The charge/discharge characteristics are shown in Fig. 8, and the life characteristics are shown in Fig. 9.

5 Comparative Example

The preparation of lithium manganese complex oxide with a spinel structure

A lithium manganese spinel was prepared by the same method as described in Example 1, except that manganese raw material that was not
10 MH-treated was used.

The application as a cathode active material and the evaluation of the characteristics of the battery

A battery was prepared by the same method as described in Example 1, except that lithium manganese spinel prepared in the above was used as a
15 cathode active material, and the characteristics of the battery were evaluated.

The charge/discharge characteristics are shown in Fig. 8, and the cyclic performance are shown in Fig. 9.

The lithium or lithium ion secondary battery using lithium manganese complex oxide with a spinel structure without defects of the present invention
20 has excellent charge/discharge characteristics and cyclic performance.

WHAT IS CLAIMED IS:

1. A method for preparing a manganese compound for a lithium manganese complex oxide, comprising the step of simultaneously applying a mechanical force and a heat energy to a manganese compound to remove
5 defects present in particles of said manganese compound, and to control the aggregation of micro particles and the shape of the aggregated particles.
2. The method for preparing the manganese compound according to claim 1, wherein a mechanical force and a heat energy are simultaneously applied to said manganese compound with adding one or
10 more kinds of preparations selected from the group consisting of LiOH, LiOH · H₂O, LiCH₃COO, LiCHO, LiCHO · H₂O, LiNO₃, and a transition metal salt having a melting point of 200 °C or less.
3. The method for preparing the manganese compound according to claim 2, wherein the amount of said preparations is 0 to 20 wt%
15 of the manganese compound.
4. The method for preparing the manganese compound according to claim 1, wherein said manganese compound is selected from the group consisting of electrolytic manganese dioxide (MnO₂; EMD), chemical manganese dioxide (MnO₂; CMD), Mn₂O₃ and Mn₃O₄.
- 20 5. The method for preparing the manganese compound according to claim 2, wherein said manganese compound is selected from the group consisting of electrolytic manganese dioxide (MnO₂; EMD), chemical manganese dioxide (MnO₂; CMD), Mn₂O₃ and Mn₃O₄.
6. The method for preparing the manganese compound
25 according to claim 1, wherein the applied mechanical force is 0.1 to 1000 dyne/cm², the range of the temperature of the applied heat energy is 50 to 200 °C, and the applied time is 5 minutes to 5 hours.
7. The method for preparing the manganese compound according to claim 2, wherein the applied mechanical force is 0.1 to 1000
30 dyne/cm², the range of the temperature of the applied heat energy is 50 to

200 °C, and the applied time is 5 minutes to 5 hours.

8. The method for preparing the manganese compound according to claim 1, wherein a manganese compound having a shape without edge parts is prepared by using an angular shaped manganese compound as a raw material and applying mechanical force and heat energy.

9. The method for preparing the manganese compound according to claim 2, wherein a manganese compound having a shape without edge parts is prepared by using an angular shaped manganese compound as a raw material and applying mechanical force and heat energy.

10. A method for preparing lithium manganese complex oxide with a spinel structure, comprising the steps of:

a) mixing

(i) a manganese compound prepared by the method comprising the step of simultaneously applying a mechanical force and a heat energy to a manganese compound to remove defects present in the particles of said manganese compound and to control the aggregation of micro particles and the shape of the aggregated particles; and

(ii) a lithium compound ; and

b) calcining the mixture prepared in said step (a).

11. A method for preparing a lithium manganese complex oxide with a spinel structure according to claim 10, wherein the (ii) lithium compound of step (a) is selected from a lithium salt group consisting of LiOH, LiOH · H₂O, LiCH₃COO, LiCHO, LiCHO · H₂O and LiNO₃.

12. A method for preparing the lithium manganese complex oxide with a spinel structure according to claim 10, wherein the temperature of calcination of said step (b) is 400 to 900 °C, and the time of calcination is 1 to 30 hours.

13. A method for preparing the lithium manganese complex oxide with a spinel structure according to claim 11, wherein the temperature

15

of calcination of said step (b) is 400 to 900 °C, and the time of calcination is 1 to 30 hours.

14. A lithium or lithium ion secondary battery comprising an anode, an electrolyte and a cathode using a lithium manganese complex oxide powder with a spinel structure as an active material, wherein said
5 active material is a lithium manganese complex oxide with a spinel structure prepared by the method comprising the steps of:

a) mixing

10 (i) a manganese compound prepared by the method comprising the step of simultaneously applying a mechanical force and a heat energy to a manganese compound to remove defects present in particles of the manganese compound and to control the aggregation of micro particles and the shapes of the aggregated particles; and

(ii) a lithium compound; and

15 b) calcining the mixture.

1/6

Fig.1

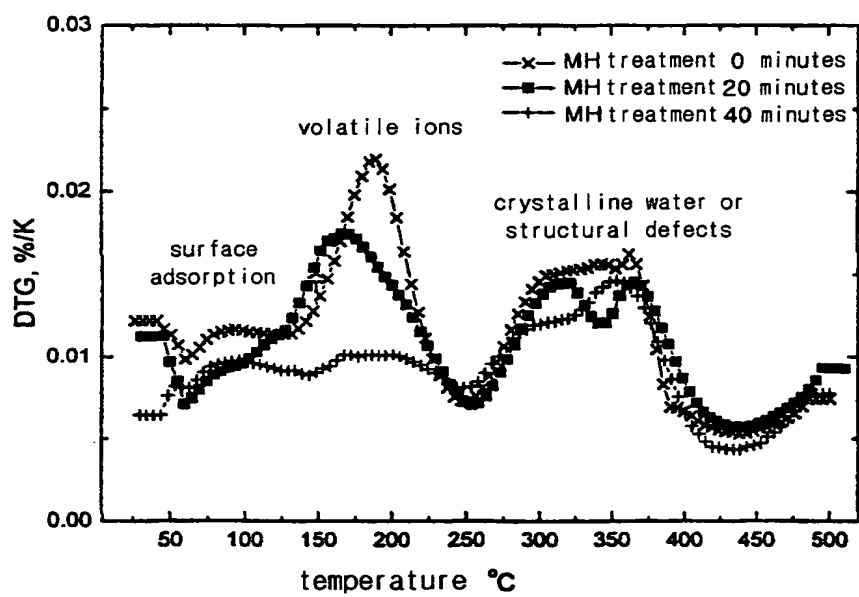
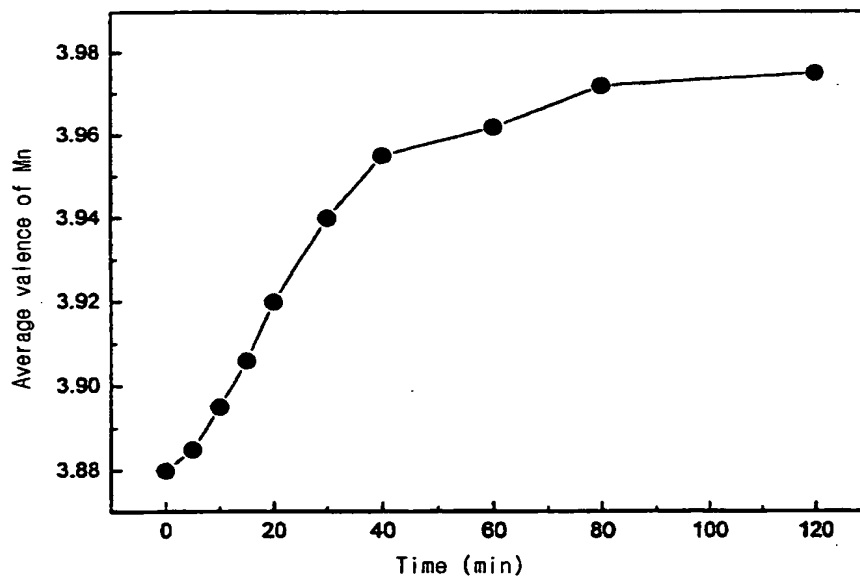


Fig.2

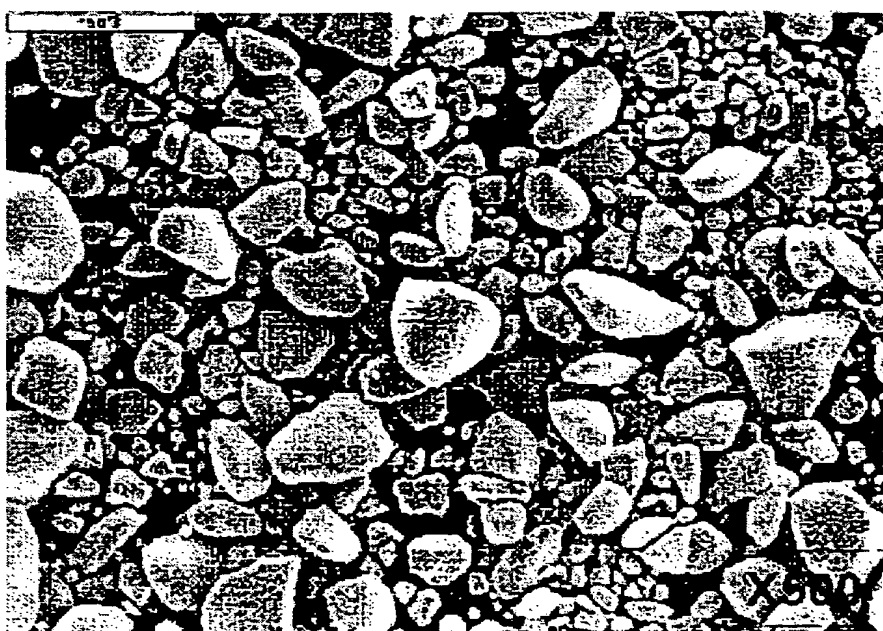


2/6

Fig.3



Fig.4



3/6

Fig.5

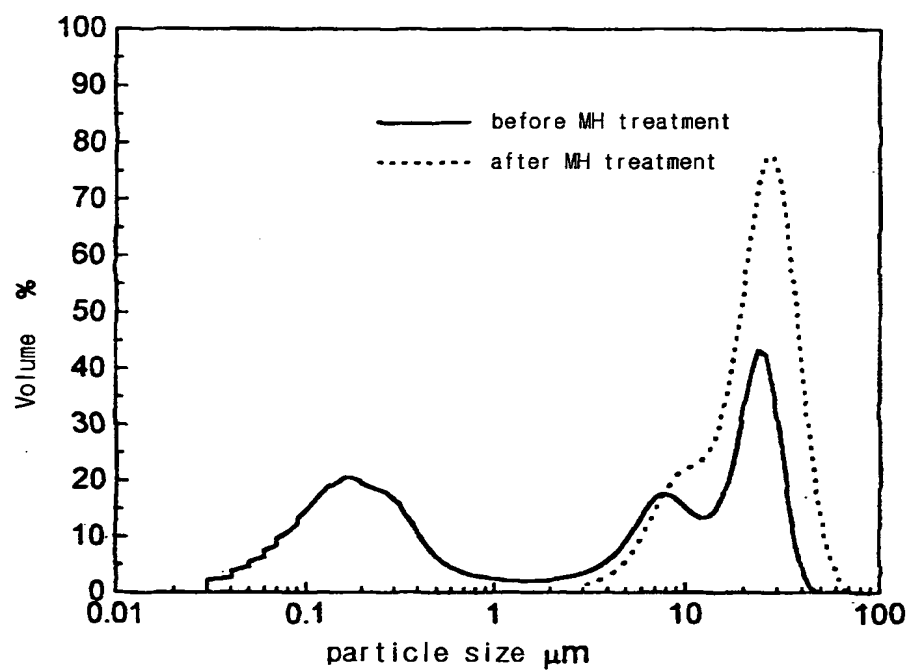
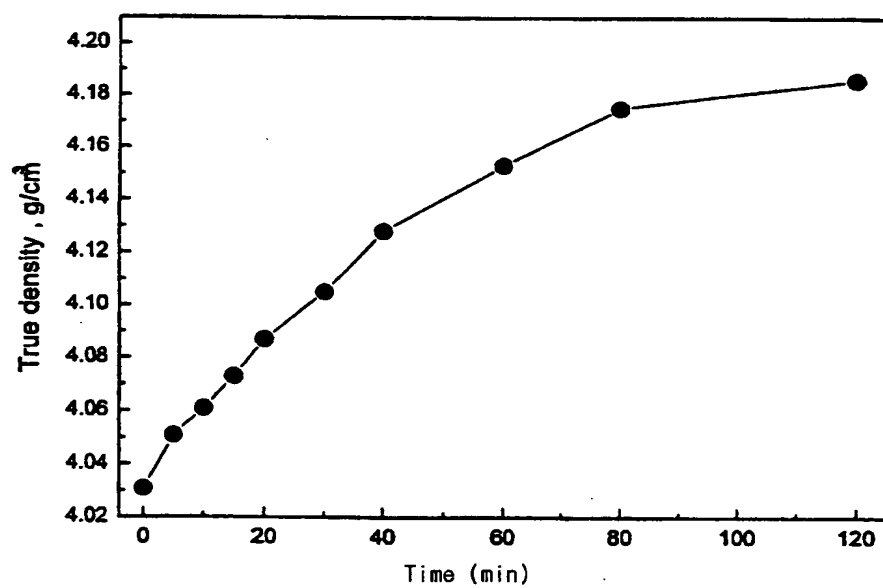
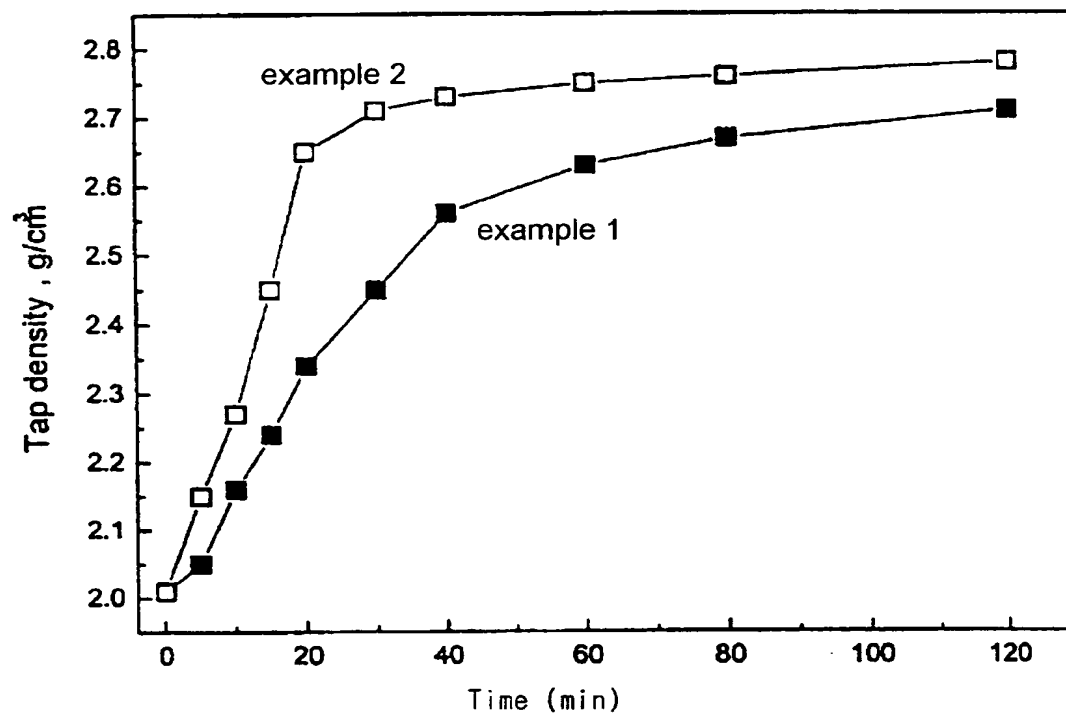


Fig.6



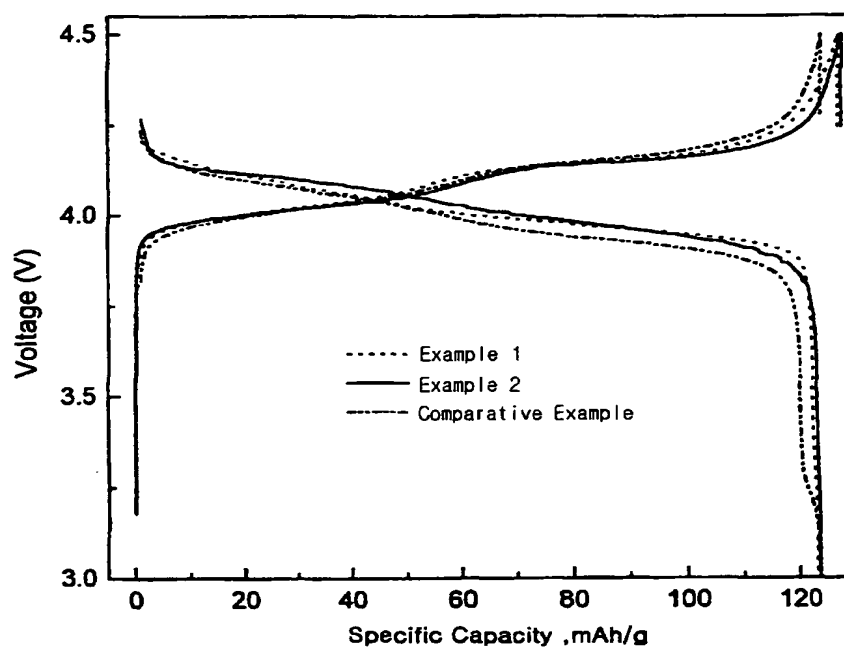
4/6

FIG. 7



5/6

Fig.8



6/6

Fig.9

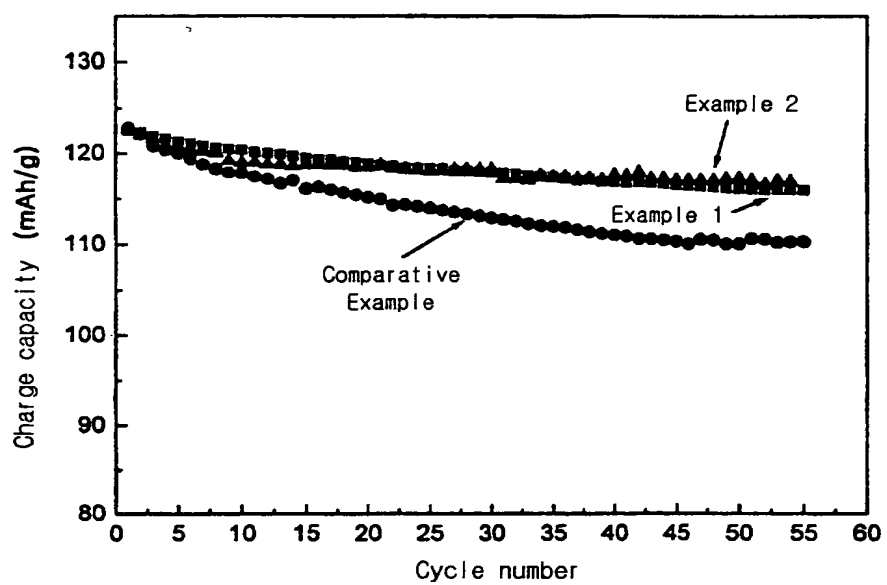


Fig.10

